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WATER MOLECULE MODELING TASK 2 OF INVESTIGATION OF GENERATION A--ETC(U)
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WATER MOLECULE MODELING TASK 2 OF
INVESTIGATION OF GENERATION AND
PROPAGATION OF INTENSE RADIATION

Optical Sciences Center
University of Arizona
Tucson, AZ 85721

December 1976

Final Report



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AIR FORCE WEAPONS LABORATORY
Air Force Systems Command
Kirtland Air Force Base, NM 87117

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This technical report has been reviewed and is approved for publication.

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SECTION I

WORK OVERVIEW

This report summarizes and references work completed on Task 2 (water molecule model) of the BOA contract number F29601-74-A-0023 between the Air Force Weapons Laboratory, Kirtland Air Force Base, and the University of Arizona Optical Sciences Center. This first section serves as an overview of the work. Section II presents information from papers published and gives abstracts of talks presented. It is followed by two sections giving greater detail on three-mode extensions and collision models, respectively; work that has not yet been submitted for publication.

Perhaps the most aesthetically satisfying way of treating the interaction of radiation with the water molecule would be to employ a Schrödinger equation for all particles involved, electrons and nuclei alike. Such ab initio calculations have been pursued at considerable time and expense elsewhere. They unfortunately require huge computer facilities and, worse still, do not produce results as accurate as those needed for purposes of the Air Force Weapons Laboratory. Hence, another approach is necessary. The current work substitutes for the electronic part of the problem a plausible phenomenology tied to experimental observations and then proceeds with a simpler quantum mechanical calculation. Specifically, least-squares fits to experimental data are made for several zero-rotational, vibrational transition frequencies predicted by solution of a phenomenological Schrödinger equation. The bending mode of the molecule is described by a Morse potential whose parameters are varied to achieve the best fit. An encompassing iterative loop is included to match, in addition, two large rotation constants to experimental data. An important feature of the method is that the vibrational-rotational energies and wave functions are determined together through matrix diagonalizations. This simultaneous diagonalization is necessary because the bending mode is strongly coupled to the rotational motion of the molecule.

by means of centrifugal distortions. The approach described here has been published in Chemical Physics Letters (see p. 4 for abstract). Aspects of the work were given as an invited paper at the IVth Winter Colloquium on Quantum Electronics (see p. 12 for abstract) and in talks at the Air Force Weapons Laboratory (see pp. 12-13 for abstracts). Extension of the model to treat the three vibrational modes (symmetric and antisymmetric stretch modes as well) is outlined in Section III of the present report, and was presented at the Air Force Weapons Laboratory (see p. 13 for abstract).

A computer study has been carried out revealing that the standard spectroscopic modeling techniques often used to treat the water molecule are inadequate except in limited spectral regimes and give an overall incorrect picture of the molecule. This study, published as AFWL Technical Report 75-84 (see p. 12 for abstract) is important, for it shows that currently the only model satisfactory for the purposes of the Air Force Weapons Laboratory is that presented here.

Section IV discusses work on calculation of the inelastic rotational relaxation cross sections of the water molecule with other atmospheric constituents. The cross sections are calculated within the semiclassical Born approximation, which is believed to be quantitatively accurate for the range of velocities and conversion energies of interest. A more detailed theory of rotational relaxation that should yield quantitatively accurate results has been published (see p. 14 for abstract).

In addition to simplicity and ease of use, the approach to molecular modeling described here promises to be easily applied to molecules other than water. It should furthermore be possible to include effects such as Coriolis forces. At this point, it is not clear how accurate refined models will be, but it may well be possible to obtain spectroscopic accuracy.

SECTION II

PAPERS PUBLISHED AND ABSTRACTS OF TALKS

This section discusses papers that have been published and gives abstracts of talks on work supported under the water molecule task:

- (1) "A Simple, Reliable Model of the Bending Mode of Water," (p. 4).
- (2) "Spectroscopic Modeling of the Water Molecule," (p. 12).
- (3) "Quantum Modeling of the Water Molecule," (p. 12).
- (4) "Molecular Spectroscopy," (p. 12).
- (5) "Molecular Vibrational Relaxation," (p. 13).
- (6) "Multimode Model of the Water Molecule," (p. 13).
- (7) "A Scaling Relationship for Inelastic Rotational Collisions and Application of the Sudden Approximation to Molecular Collisions," (p. 14).

"A Simple, Reliable Model of the Bending Mode of Water"¹

ABSTRACT

A simple, reliable model of the bending mode vibration of the water molecule based on the Morse oscillator is presented. The model yields accurate predictions of the rotation-vibration level structure in the various bending mode bands as well as the geometric structure of the ground state.

Due to its unique rotation-vibration structure and its dominant role in atmospheric absorption of CO₂ laser radiation, the H₂¹⁶O molecule has recently been a topic of great interest. The internal nuclear motion of the molecule is substantially complicated by the following four features: (1) the large molecular asymmetry; (2) the small moments of inertia (and correspondingly large rotational energies); (3) the extreme anharmonic and low frequency structure of the bending mode vibrations; and (4) the large amplitude fluctuations of the bond angle. These features cause water to display strong coupling between the molecular rotations and the bending mode vibration, and in addition, to exhibit large centrifugal distortion effects. These effects manifest themselves not only in the rotation-vibration energy level scheme of water but also in its effective geometric structure. For example, examination of recent high resolution microwave data reveals that the apparent bond angle deviates over a range of 3.4° depending on which pair of (experimentally determined) inertia constants are used in the analysis. In addition, it appears that spectroscopic techniques based on purely rotational Hamiltonians are not capable of describing the rotational level structure in the bending mode bands. Thus, from the viewpoints of both physics and chemistry, there is need for a simple, reliable model of the water molecule that can be used to calculate electrodynamic properties and collision rates as well as the rotation-vibration level schemes and geometric structure.

¹Published as D. Rogovin, M. Sargent III, and H. Tigelaar, Chem. Phys. Letters 30, 400, 1975.

From the discussion above it is clear that such a model demands (1) an accurate description of the bending vibration, and (2) a non-perturbative treatment of the coupling between this vibrational mode and the molecular rotations. In this report such a model of the water molecule is presented. The model accurately describes the energy level structure in the ground and first excited bending mode bands. Furthermore, it predicts a ground state geometric structure in good agreement with experiment. In addition, it is moderately successful in describing the rotational states in the (020) band. This represents significant improvement over previous work which, although more accurate over a limited spectral range, fails entirely outside that range.

The model considers only fluctuations in the bond angle and the coupling of the bending mode to the molecular rotations. On physical grounds one expects these features to be of greatest importance in determining the molecular characteristics of water in these bands. Due to the strength of the OH-bond, the zero point fluctuations of the symmetric and asymmetric stretch modes are quite small, and hence do not significantly affect the molecular structure of $H_2^{16}O$. Furthermore, additional interactions such as Coriolis forces, vibrational angular momentum, and other forms of mode-mode couplings are of lesser importance and are ignored. Finally, the goal of this work is not to achieve spectroscopic accuracy, but rather to provide a model of the water molecule that reliably describes the bending mode vibrations. Such a model can serve as a foundation for determining the water molecule's structure and role in atmospheric absorption of CO_2 laser radiation. An additional advantage is that the approach is applicable to other asymmetric rotors as well.

This model involves a self-consistent fit to the first three experimentally determined vibrational spacings (in the $J = 0$ rotational states) and two ground state rotation constants. As such, it is not an *ab initio* calculation, but has the distinct advantages of greatly reduced numerical computation and increased accuracy.

The basic approach is to first determine the $J = 0$ vibrational eigenfunctions and eigenvalues as well as the static geometric structure

of the water molecule. This consists of iterating the following three steps in a self-consistent fashion:

(1) The vibrational eigenfunctions and eigenvalues are determined by solving the Schroedinger equation for the bending mode vibration. Because the experimentally measured $J = 0$ vibrational spacings are quite anharmonic, the bending mode is modelled by means of a Morse oscillator potential. As the moment of inertia associated with the bending mode depends only weakly on fluctuations of the bond angle, the following Schroedinger equation (for $\theta > 0$) is used to describe the bending mode

$$\left[\frac{\hbar^2}{2I} \frac{\partial^2}{\partial \theta^2} + B_0 \{1 - \exp[-\beta(\theta - \theta_0)]\}^2 \right] u_\nu(\theta) = E_\nu u_\nu(\theta) \quad (1)$$

where θ is the instantaneous bond angle, $u_\nu(\theta)$ and E_ν being the eigenfunction and eigenvalue, respectively, for the $(0\nu 0)$ state. The system is symmetric about the linear configuration (i.e., $\theta = 0$), although the magnitude of the potential at this angle, $B_0[1 - \exp(\beta\theta_0)]^2$, ensures that $u_\nu(0)$ is essentially zero. In equation (1) the angle θ_0 is the "bare" bond angle, i.e., the geometric bond angle assumed in the absence of all vibrational effects. The moment of inertia

$$I = m_H r_0^2 [m_O + m_H(1 + \cos\theta)] / m_{H_2O}$$

is evaluated at θ_0 , which is computed in step (3) below. The quantities m_H , m_O , and m_{H_2O} are the masses of atomic hydrogen, atomic oxygen and the water molecule, respectively. The effective bond length r_0 is defined below in step (3). The quantities B_0 and β determine the height and the range of the potential. The solution of equation (1) is that of the Morse oscillator. Varying the Morse parameters B_0 and β , we fit the first three zero-rotation, bending mode vibrational energy level spacings to the experimental values of 1594.5 cm^{-1} , 1556.94 cm^{-1} , and 1515.25 cm^{-1} . The fit produces accuracies within 0.5 to 1.5 cm^{-1} for the first three level spacings (other more complicated models used yielded fits within one cm^{-1} for all three; these models included the effects of an angle-dependent moment of inertia in their kinetic energy).

(2) Using the first four vibrational eigenfunctions so derived, we calculate the matrix elements for the rotation constants A , B , and C (matrix elements of the reciprocals of the moments of inertia about the principal axes), and the matrix elements of the bond-angle fluctuation moments, $\langle \delta\theta^n \rangle = \langle (\theta - \theta_0)^n \rangle$.

(3) The A and B rotation constants are then expanded in terms of these moments and the resulting transcendental equations are solved for the bare bond angle θ_0 and an effective bond length $r_0 \equiv (\langle G | 1/r^2 | G \rangle)^{-1/2}$, where $|G\rangle$ represents the ground state stretch modes and r is the instantaneous bond length. Thus, r_0 and θ_0 yield the best possible values of the ground state A and B rotation constants.

Note that this procedure ignores all correlations between the bending mode vibration and the stretch modes. Finally, steps (1) through (3) are repeated until self-consistent energy eigenvalues and bond angles are obtained. Note also that this process can be generalized to include many vibrational modes as well as mode-mode correlations and is a convenient technique for obtaining geometric molecular structure from spectral data.

The following values were derived for the Morse oscillator model

$$\begin{aligned} B_0 &= 33740 \text{ cm}^{-1}, & \beta &= 1.0095 \text{ \AA}^{-1}, \\ \theta_0 &= 103.8^\circ, & r_0 &= 0.962 \text{ \AA}. \end{aligned}$$

These did not deviate significantly from results of other more complex models, e.g., θ_0 differs by approximately 0.1° from a five-parameter model, which included an angle dependent moment of inertia.

The average bond angle $\langle \theta \rangle$ defined by

$$\langle \theta \rangle = \theta_0 + \langle \delta\theta \rangle \quad (2)$$

is found to be 104.8° , which is in agreement with the effective experimental value. The fact that $\langle \delta\theta \rangle \sim 1^\circ$ indicates that the bending mode potential is highly anharmonic. In addition, the zero point fluctuations amount to approximately 6.4° . Finally, the effective bond length lies within 0.003 \AA of the effective experimental value.

Having determined the self-consistent, zero-rotation, vibrational eigenfunctions and eigenvalues, and the corresponding rotation constants, the vibration-rotation energies and wave functions are then calculated using a modified theory of the asymmetric rotor. Specifically, the vibrational-rotational energies are diagonalized together, *not* individually as is usually done. This combined diagonalization is particularly important for H₂O, inasmuch as the rotation-vibration interaction is extremely strong and consequently plays an important role in the rotation-vibration level structure. A measure of the strength of the rotation-vibration coupling is given by the ratio of the off-diagonal matrix elements of the inverse of the moment of inertia to its equilibrium value. In particular, for the Morse oscillator model, (I_{xx} is the moment of inertia operator about the A-rotation axis)

$$\frac{|\langle 000 | 1/I_{xx} | 010 \rangle|}{|\langle 000 | 1/I_{xx} | 000 \rangle|} \sim 0.15 \quad (3)$$

Table 1 compares theoretical and experimental values for 43 rotational levels in the ground vibrational state. Typical accuracies are on the order of 1% or better. The success of the model is perhaps best illustrated by the 10₉ level whose observed rotational energy is 2702 cm⁻¹, almost twice the bending mode energy. This state experiences considerable distortion inasmuch as the rigid rotor energy is 2909 cm⁻¹. Because the theoretical value of 2730 cm⁻¹ is correct to within 1%, this indicates that the model accurately describes nonrigid effects that arise from fluctuations of the bond angle. Note also that numerous states have rotational energies considerably greater than 1000 cm⁻¹, all of which are described well by the model.

Table 2 compares corresponding values for 35 rotational levels in the (010) band. The situation is similar to the ground vibrational state. Note that the only experimental information used for this band is the $J = 0$ vibrational spacings to the ground, 2v₂ and 3v₂ states. These results are indicative of the essential validity of our approach.

Table 1
COMPARISON OF THEORETICAL AND EXPERIMENTAL VALUES FOR
ROTATIONAL ENERGY LEVELS IN GROUND VIBRATIONAL STATES

<i>V</i>	<i>J</i>	τ	Theoretical energy (cm ⁻¹)	Experimental energy (cm ⁻¹)	Percent error
0	1	1	42.48	42.37	<0.01
0	2	0	95.35	95.17	+0.19
0	2	+2	136.56	136.15	+0.30
0	3	-3	137.99	136.77	+0.89
0	3	0	207.19	206.28	+0.43
0	3	3	287.21	285.40	+0.62
0	4	-4	224.43	222.04	+1.07
0	4	-1	301.95	300.38	+0.52
0	4	+1	384.76	382.49	+0.59
0	4	3	492.70	488.16	+0.93
0	5	-3	401.91	399.45	+0.61
0	5	0	506.83	504.00	+0.56
0	5	2	615.85	610.12	+0.94
0	5	4	752.85	742.10	+1.40
0	6	-4	547.08	542.87	+0.78
0	6	-2	606.49	602.67	+0.63
0	6	1	762.82	756.76	+0.80
0	6	3	901.34	888.67	+1.43
0	6	6	1069.54	1045.15	+2.33
0	7	-5	710.91	704.20	+0.95
0	7	-2	822.76	816.65	+0.75
0	7	+1	938.61	931.23	+0.79
0	7	3	1072.11	1059.89	+1.15
0	7	5	1242.56	1216.39	+2.15
0	8	-7	755.61	744.14	+1.46
0	8	-5	894.94	885.64	+1.05
0	8	-3	1014.91	1006.14	+0.87
0	8	-1	1132.43	1122.78	+0.86
0	8	1	1269.21	1255.19	+1.12
0	8	6	1636.68	1590.70	+2.89
0	9	-9	934.34	920.20	+1.54
0	9	-7	1092.47	1079.16	+1.23
0	9	-5	1214.85	1202.04	+1.07
0	9	-3	1295.92	1283.02	+1.01
0	9	-1	1372.31	1360.56	+0.86
0	9	1	1492.15	1477.46	+1.06
0	9	3	1658.11	1631.58	+1.64
0	9	5	1851.13	1810.76	+2.23
0	10	-8	1310.00	1293.22	+1.30
0	10	-5	1463.28	1446.23	+1.18
0	10	0	1744.22	1724.80	+1.13
0	10	4	2099.77	2054.55	+2.20
0	10	9	2730.31	2702.09	+1.03

Table 2
COMPARISON FOR FIRST EXCITED VIBRATIONAL LEVEL

<i>V</i>	<i>J</i>	τ	Theoretical energy (cm ⁻¹)	Experimental energy (cm ⁻¹)	Percent error
1	1	0	39.90	40.35	+1.12
1	2	-2	70.28	70.34	-0.06
1	2	1	146.59	147.92	-0.90
1	3	-3	137.80	137.33	+0.34
1	3	-1	175.14	177.71	-1.47
1	3	3	310.04	313.12	-0.98
1	4	-4	224.82	222.76	+0.93
1	4	-1	311.17	313.35	-0.70
1	4	4	533.77	535.01	-0.23
1	5	-5	330.19	326.11	+1.25
1	5	-3	402.93	406.21	-0.81
1	5	0	527.49	531.85	-0.82
1	5	3	656.14	657.08	-0.14
1	5	5	816.65	811.65	+0.61
1	6	-3	565.63	566.72	-0.16
1	6	0	680.37	687.97	-1.10
1	6	4	964.18	958.39	+0.99
1	7	-6	596.75	586.68	+1.72
1	7	-3	788.95	797.79	-1.11
1	7	3	1130.70	1129.71	+0.08
1	7	7	1555.53	1515.43	+2.63
1	8	-4	994.92	1001.31	-0.54
1	8	0	1165.04	1170.16	-0.44
1	8	4	1518.96	1506.69	+0.81
1	9	-7	1099.75	1093.67	+0.53
1	9	0	1542.97	1545.06	+0.14
1	9	5	1963.73	1932.18	+2.15
1	9	9	2513.03	2399.80	+4.72
1	10	-8	1319.00	1320.76	-0.13
1	10	-5	1479.14	1478.36	<0.01
1	10	0	1788.10	1793.08	-0.28
1	10	4	2211.04	2176.36	+1.55
1	10	6	2463.60	2403.21	+2.51
1	10	8	2694.28	2646.41	+1.80

Finally, in table 3, results for 25 levels in the (020) band are compared to the experimental values. The discrepancies here are somewhat larger and arise for several reasons; namely, (1) a Fermi resonance between this vibrational state and the v_1 state, (2) the least squares fit to the $J = 0$ vibrational spacings was poorest for this state, and (3) Coriolis forces are clearly of more importance here.

Table 3
COMPARISON FOR SECOND VIBRATIONAL STATE

V	J	τ	Theoretical energy (cm^{-1})	Experimental energy (cm^{-1})	Percent error
2	1	-1	23.58	23.87	-1.21
2	2	-2	69.92	70.53	-0.86
2	2	+2	159.02	165.47	-3.89
2	3	-3	137.48	137.74	-0.19
2	3	0	228.94	236.27	-3.08
2	3	3	338.08	348.97	-3.09
2	4	-4	225.10	223.77	+0.59
2	4	-1	322.71	330.47	-2.37
2	4	4	582.00	595.27	-2.06
2	5	-5	331.07	327.57	+1.06
2	5	-3	404.21	413.97	-2.36
2	5	0	553.49	567.67	-2.49
2	5	5	891.98	901.27	-1.03
2	6	-6	455.73	448.87	+1.53
2	6	-2	614.28	632.77	-2.76
2	6	4	1039.86	1045.87	-0.06
2	6	6	1263.35	1259.57	+0.03
2	7	-7	598.47	587.07	+1.98
2	7	-3	791.06	815.87	-3.04
2	7	0	1012.95	1036.27	-2.25
2	8	-8	759.94	742.87	+2.30
2	8	-5	914.60	920.07	-0.59
2	8	-1	1207.31	1232.37	-2.03
2	9	-9	939.90	917.27	+2.46
2	9	-7	1108.69	1115.17	-0.58

"On Spectroscopic Modeling of the Water Molecule"²

ABSTRACT

An examination has been made of the validity of spectroscopic modeling techniques for describing the rotational structure of high-lying rotational levels of light asymmetric rotators such as water. The present techniques based on Watson's rotational Hamiltonian are inadequate.

"Quantum Modeling of the Water Molecule"³

ABSTRACT

A model of the water molecule that correctly predicts the rotational-vibrational properties in the ground electronic state is presented. Comparison with other models, particularly to spectroscopic models, is made.

"Molecular Spectroscopy"⁴

ABSTRACT

Molecular spectroscopy is a broad area easily complicated by the large number of different molecular systems. Such topics as the rotation-vibration Hamiltonian, molecular energy level structure, and techniques for calculating the rotation-vibration structure of molecular systems are discussed.

²To be published as D. Rogovin and H. Tigelaar, AFWL TR-75-84, 1975.

³Talk given by D. Rogovin at the Air Force Weapons Laboratory, Kirtland Air Force Base, on May 31, 1974.

⁴Talk given by D. Rogovin at the Air Force Weapons Laboratory, Kirtland Air Force Base, on October 8, 1974.

"Molecular Vibrational Relaxation"⁵

ABSTRACT

Molecular vibrational relaxation processes are of extreme importance. A convenient technique for calculating the cross sections that are associated with such processes has recently been developed at the University of Arizona. This technique is discussed along with its advantages over conventional approaches.

"Multimode Model of the Water Molecule"⁶

ABSTRACT

A model of the water molecule that treats in a nonperturbative fashion all three vibrational modes is presented. Advantages and need for such an approach are discussed.

⁵Talk given by D. Rogovin at the Air Force Weapons Laboratory, Kirtland Air Force Base, on October 9, 1974.

⁶Talk given by D. Rogovin and M. Sargent III at the Air Force Weapons Laboratory, Kirtland Air Force Base, on January 9, 1975.

"A Scaling Relationship for Inelastic Rotational Collisions and Application of the Sudden Approximation to Molecular Collisions"⁷

ABSTRACT

The sudden approximation is applied to inelastic rotational collisions that arise from the long range multipole potential and compared to experiment with reasonably accurate results. In addition it is shown that the cross section must obey certain scaling relations.

In this report the sudden approximation is applied to calculate the total inelastic scattering cross section due to rotational collisions that arise between two rigid dipolar molecules. In addition, it is shown that for strong collisions (i.e., cases for which the Born or semiclassical Born approximation is not valid) the inelastic cross section has a certain scaling property, which is discussed at the end of this report. Note that strong collisions involving the conversion of rotational energy to thermal motion are of importance in understanding the propagation of intense laser light through the atmosphere. Reported here are preliminary results that were applied to simple systems on which experimental data are available. Extensions to water are being considered. The sudden approximation has been applied by Kramer and Bernstein (ref. 1) to atom-molecule systems, but has not yet been employed for collisions between molecular systems. The sudden approximation is essentially semiclassical in nature with the center-of-mass motion of the colliding molecules taken to be a straight-line path characterized by an impact parameter b . Due to its computational ease, the sudden approximation is particularly convenient for obtaining inelastic cross sections for strong collisions between molecular systems. It pays for this simplicity by neglecting the finite energy level spacings that quantum mechanical rotors display, thus treating all collisions as resonant collisions. As a result the sudden approximation tends to overestimate the size of the collision

⁷Paper published as D. Rogovin, J. Phys. B: Atom. Molec. Phys. 7, L317, 1974.

cross section. On physical grounds, one expects that whenever the parameter χ satisfies the inequality

$$\chi = \frac{|\omega|b}{v} \geq 1 \quad (1)$$

serious difficulties will arise. In equation (1) $\hbar|\omega|$ is the amount of energy converted from rotational to translational motion (or vice versa) in a given collision. v is the initial relative velocity between the colliding molecules. Physically, χ is the ratio of the time in which the molecules are in range of one another (b/v) versus the time it takes to make the transition between the states of interest, i.e., $1/\omega$.

Next, the total inelastic scattering cross section within the sudden approximation is derived. For two rigid dipoles the long-range angle-dependent interaction potential is given by

$$V(\vec{R}; \vec{r}_1, \vec{r}_2) = -4\pi \left(\frac{8\pi}{15}\right)^{1/2} \frac{p_1 p_2}{R^3} \sum_{m_1, m_2 = -1}^1 C(112, m_1, m_2, m_1 + m_2) \cdot Y_1^{m_1}(\vec{r}_1) Y_1^{m_2}(\vec{r}_2) Y_2^{m_1 + m_2}(\vec{R})^* \quad (2)$$

where it is assumed that each of the molecules possesses at least a three-fold axis of symmetry. In equation (2) $C(112, m_1, m_2, m_1 + m_2)$ is a Clebsch-Gordon coefficient, \vec{R} is the vector distance between the molecular centers of mass, and $p_1(p_2)$ is the dipole moment of molecule 1(2) with internal coordinates $r_1(r_2)$. Restricting the calculation to diatomics and denoting the initial and final rotational states by $|J_1 M_1, J_2 M_2\rangle$ and $|J_1' M_1', J_2' M_2'\rangle$, it is found for the probability that the collision brings the system from the initial (unprimed) state to the final (primed) state*

$$|\langle J_1' M_1' J_2' M_2' | T(\vec{b}) | J_1 M_1 J_2 M_2 \rangle|^2 = |\langle J_1' M_1', J_2' M_2' | e^{i\delta(\vec{k}_1, \vec{k}_2, \vec{b})} | J_1 M_1, J_2 M_2 \rangle|^2 \quad (3)$$

*The normalization condition for all possible collisions is

$$\sum_{\text{all final states}} |\langle J_1' M_1', J_2' M_2' | T | J_1 M_1, J_2 M_2 \rangle|^2 = 2.$$

where the phase shift $\delta(\vec{r}_1, \vec{r}_2; \vec{b})$ for straight-line paths is

$$\delta(\vec{r}_1, \vec{r}_2; \vec{b}) = -\frac{1}{\hbar v} \int_{-\infty}^{\infty} dz V(b; z; \hat{\vec{r}}_1, \hat{\vec{r}}_2).$$

For dipole-dipole collisions, this phase shift is equal to

$$= \frac{p_1 p_2}{\hbar v b^2} \sin\theta_1 \sin\theta_2 \cos(\phi_1 + \phi_2 - 2\phi) \quad (4)$$

where the quantity $(p_1 p_2 / \hbar v b^2)$ is the ratio of the time in which the molecules are in range of one another versus the time it takes for the potential to scatter the molecules. The total inelastic scattering cross section is given by

$$\begin{aligned} \sigma_T^{\text{inelastic}} &\times \int_0^{2\pi} d\phi \int_0^{\infty} db b \sum_{\substack{J_1'M_1', J_2'M_2' \\ \text{initial state}}} \sum_{\substack{\vec{r}_1, \vec{r}_2 \\ |J_1M_1, J_2M_2|}} \\ &| \langle J_1'M_1', J_2'M_2' | e^{i\delta(\vec{r}_1, \vec{r}_2; \vec{b})} | J_1M_1, J_2M_2 \rangle |^2 \\ &= \int_0^{2\pi} d\phi \int_0^{\infty} db b \{ 1 - | \langle J_1M_1, J_2M_2 | \\ &e^{i\delta(\vec{r}_1, \vec{r}_2; \vec{b})} | J_1M_1, J_2M_2 \rangle |^2 \} \quad (5) \end{aligned}$$

which is identical to the expression that Glauber (ref. 2) has derived. If the short-range portion of the interaction is treated as a hard-core potential of radius b^* , then

$$\begin{aligned} \sigma_T^{\text{inelastic}} &= \pi b^{*2} + 2\pi \int_{b^*}^{\infty} db b \{ 1 - | \langle J_1M_1, J_2M_2 | \\ &e^{i\delta(\vec{r}_1, \vec{r}_2; \vec{b})} | J_1M_1, J_2M_2 \rangle |^2 \} \quad (6) \end{aligned}$$

From the structure of equation (6) it is easy to show that the total inelastic cross section is a function of a single parameter Z .

$$Z = \frac{p_1 p_2}{\pi v b^*^2} \quad (7)$$

In figure 1 we have plotted the quantity $\sigma_T^{\text{inelastic}}(Z)/\pi b^*^2$ as a function of Z . For small values of Z , i.e., $Z \ll 1$, it is found that

$$\frac{\sigma_T^{\text{inelastic}}(Z)}{\pi b^*^2} \sim Z^2 \quad (8)$$

as one would expect, because this is the region where the semiclassical Born approximation is valid. For $Z \geq 2$, a numerical plot shows that

$$\frac{\sigma_T^{\text{inelastic}}(Z)}{\pi b^*^2} \sim Z \quad (9)$$

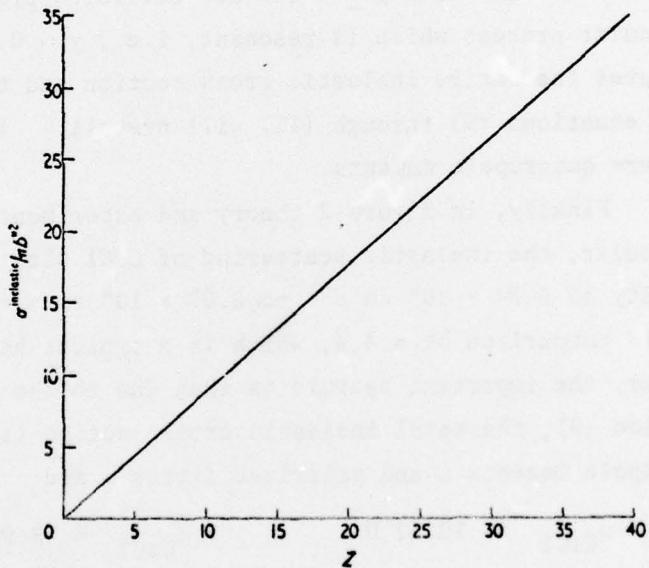


Figure 1. A plot of $\sigma_T^{\text{inelastic}} / \pi b^*^2$ against Z .

On physical grounds it is expected that the cross section will scale in this fashion for strong collisions (by strong collisions we mean cases for which first-order perturbation theory is invalid) because the probability for an elastic collision will be unity for impact parameters

greater than b^* . Note, on the basis of these considerations, that strong dipole-quadrupole collisions will scale by means of

$$\frac{\sigma_T^{\text{inelastic}}(Z)}{\pi b^{*2}} \sim Z^{2/3} \quad \text{for} \quad Z \sim \frac{PQ}{\hbar v b^{*3}} \gg 1 \quad (10)$$

and for a strong quadrupole-quadrupole collision

$$\frac{\sigma_T^{\text{inelastic}}}{\pi b^{*2}} \sim m^{1/1} \quad \text{for} \quad Z \sim \frac{QQ'}{\hbar v b^{*4}} \gg 1 \quad (11)$$

(For the case in which $\chi > 1$ for all collision processes, except for a particular process which is resonant, i.e., $\chi \sim 0$, then this process dominates the entire inelastic cross section and the same scaling relations as in equations (9) through (11) will prevail.) In equations (10) and (11), Q, Q' are quadrupole moments.

Finally, in figure 2 theory and experiment are compared. In particular, the inelastic scattering of CsCl with that of NO over a velocity of $5.34 \times 10^4 \text{ cm s}^{-1}$ to $8.07 \times 10^4 \text{ cm s}^{-1}$ (ref. 3) is compared. In this comparison $b^* = 4 \text{ \AA}$, which is a typical hard-core collision radius. However, the important feature is that due to the scaling relation, i.e., equation (9), the total inelastic cross section is independent of b^* .

The dipole moments μ and polarizabilities α are

$$\begin{array}{ll} \mu_{\text{CsCl}} = 10.42 \text{ D} & \alpha_{\text{CsCl}} = 5.912 \text{ cm}^3 \\ \mu_{\text{NO}} = 0.16 \text{ D} & \alpha_{\text{NO}} = 1.70 \text{ cm}^3 \end{array}$$

Unfortunately, the experimental data points also include the elastic scattering which we cannot estimate. The theory overestimates the scattering cross sections by about 20%. This discrepancy arises from the finite energy spacing (for NO the rotation constant is $\sim 5.1 \times 10^4 \text{ MHz}$) and also from the large polarizabilities of CsCl and NO.

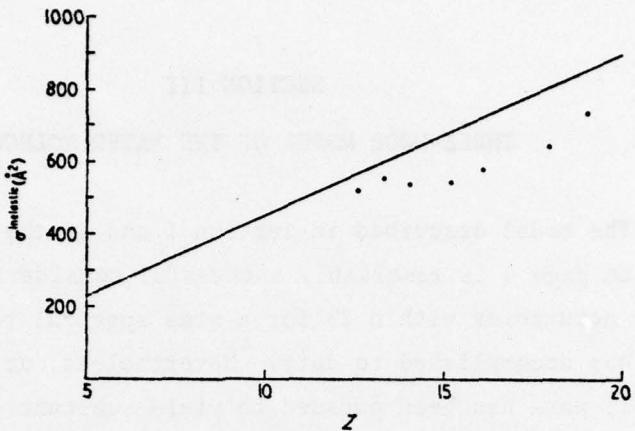


Figure 2. Comparison of theory with experiment for the range $v = 5.34 \times 10^{-4}$ to 8.07×10^4 cm s^{-1} . $p_1 = 10.42 \text{ D}$, $p_2 = 0.16 \text{ D}$, $b^* = 4 \text{ Å}$.

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SECTION III

THREE-MODE MODEL OF THE WATER MOLECULE

The model described in section I and in the paper whose abstract appears on page 4 is remarkably successful considering its simplicity. It achieves accuracies within 2% for a wide spectral region, a feat that only it has accomplished to date. Nevertheless, at the cost of complicating the model, work has been pursued to yield substantially greater accuracy. In particular, the model has been extended to treat the symmetric and antisymmetric vibrational stretch modes in addition to the vibrational bending mode. This is the first time three modes have been treated with any approach. This section discusses the principal features of that extension.

The basic least-squares approach is the same as described in section I. An approximate Hamiltonian treating atom-atom interactions and kinetic energies for the three particles is chosen. The atom-atom interactions are described by Morse potentials having a total of four adjustable parameters (two for the H-H interaction and two for the H-O interactions). The matrix for the Hamiltonian is calculated on a basis consisting of products of Morse oscillator eigenfunctions. These eigenfunction products span the triple direct product space of the three-mode problem. The matrix is hence a multidimensional one, but with the use of some intricate subscripting algorithms can be formally written and treated as a two-dimensional matrix. It is then diagonalized, and appropriate differences of the eigenvalues are fitted to experimentally observed transition frequencies in much the same way as for the single-mode case.

The extension to three modes is in large part applicable to the N mode problem. The terms defining the Hamiltonian must be written for any specific molecule, and the subscripting algorithms have to be modified appropriately. As such, other molecules of importance for atmospheric propagation of laser radiation can be treated with modifications of the

model. Work is currently under way to finish the implementation of this model for the water molecule and then to consider other molecules like deuterated water, ozone, and eventually methane.

SECTION IV

INELASTIC ROTATIONAL COLLISIONS OF WATER VAPOR WITH OTHER ATMOSPHERIC MOLECULES

Inelastic rotational collisions of water vapor with other atmospheric molecules are of great importance for the propagation of laser radiation through the atmosphere. These processes give rise to a conversion of laser energy into kinetic motion and consequently must be thoroughly understood. The collision events of greatest significance are water with oxygen, with nitrogen, and to a lesser degree, with itself. These processes all arise from the long-range electrostatic multiple interactions. The first two cases are dominated by dipole-quadrupole interactions, whereas the last arises from the dipole-dipole interaction. In addition, quadrupole-quadrupole forces as well as induction forces play a role in all these processes.

Collision processes of such complexity must be analyzed in a sequence of steps. Accordingly, computer programs have been designed and executed that treat the lowest order rigid multipole interactions within a unitarized semiclassical Born approximation. Such interactions clearly dominate these molecular collision processes, and the semiclassical Born approximation is known to give qualitatively reliable cross sections providing it is unitarized. The investigation indicates that the cross sections of interest are on the order of 50 square Angstroms. Such values are quite reasonable. The programs include subroutines for calculating both Clebsch-Gordon coefficients as well as dipole moment matrix elements. These quantities are required for calculating other electrodynamic properties of water, such as absorption of radiation.

To improve the results and obtain qualitatively more reliable cross sections, a theory is being developed based on the sudden approximation. This approach takes into account the large molecular rotational energies that arise in water. One paper dealing with this subject has been published (see page 14 for abstract).